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Mechanisms of transformation of polychlorinated diphenyl ethers into polychlorinated dibenzo-*p*-dioxins and dibenzofurans

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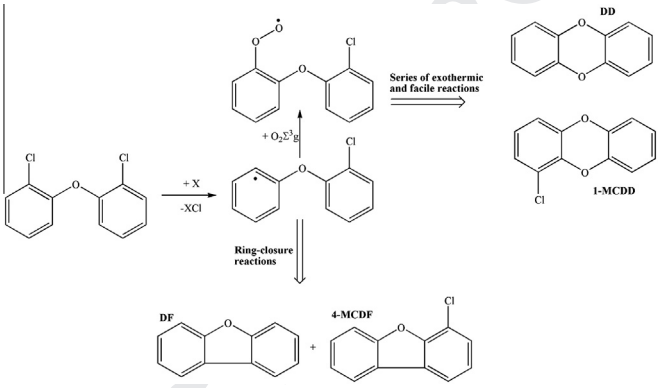
HIGHLIGHTS

- Mechanistic and kinetics study is carried out on formation of PCDD/Fs from PCDEs.
- Unimolecular decomposition pathways are found to incur high activation enthalpies.
- An *ortho* peroxy-type adduct evolves via a series of exothermic reactions to yield PCDDs.
- Reactions with H and Cl radicals results in the breakage of the ether linkage.

GRAPHICAL ABSTRACT



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ABSTRACT

This study presents a detailed mechanistic account of the formation of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) from polychlorinated diphenyl ethers (PCDEs). It applies the recently developed meta hybrid M06-2X functional and deploys the 2′-dichlorodiphenylether (2,2′-DCDE) molecule as a representative model compound for all PCDEs congeners. We find that, exceedingly high activation enthalpies prevent the direct formation of PCDFs from PCDEs via unimolecular elimination of HCl or Cl_2. Rather, loss of an *ortho* H/Cl atom initiates the transformation of PCDEs into PCDD/Fs. Subsequent formation of PCDFs takes place through ring-closure reactions with modest activation enthalpies, whereas the addition of a ground state oxygen molecule at an apparent *ortho* radical site of a PCDE congener commences a complex, yet very exothermic, mechanism leading to the formation of PCDDs. Splitting the ether linkage through H/Cl addition at the pivot carbon constitutes a major source for the formation of chlorophenoxy radicals and chlorobenzene molecules. Our kinetic and mechanistic analyses demonstrate that, the degree and pattern of chlorination of PCDEs display a negligible effect on the formation pathways of PCDD/Fs from PCDEs.

1. Introduction

Polychlorinated diphenyl ethers (PCDEs) comprise a category of persistent organic pollutants (POPs), with significant concentration levels of PCDEs consistently detected in various environmental matrices (Koistinen, 2000). Owing to their toxic and bio-accumulative properties (Bocio et al., 2003), PCDEs remain in the centre of mounting environmental and health concerns. These species form mainly as unwanted by-products during technical synthesis of chlorinated phenols and phenoxyacetic acid pesticides (Domingo, 2006). Their widespread detection has sparked a great deal of research aiming to understand emission of PCDEs from combustion

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processes, including uncontrolled fires, and their subsequent deposition in the environment. Consensus of opinion has emerged in the literature that, all thermal processes involving chlorine display propensity to generate PCDEs (Nevalainen et al., 1994; Niimi et al., 1994; Nito et al., 1997).

For instance, Kurz and Ballschmiter (1995) measured concentrations of PCDEs to be as high as 93.0 μg/(kg fly ash) in a typical municipal waste incinerator (MWI). Recent experimental studies have targeted homogenous and heterogeneous formation of PCDEs from condensation of potent precursors. Liu et al. (2008) investigated the gas-phase formation of PCDEs via condensation of chlorinated phenols and benzenes, and reported that co-pyrolysis of pentachlorophenol with polychlorobenzenes leads predominantly to the formation of highly chlorinated congeners of PCDEs. Along the same line of enquiry, oxidation of chlorinated phenols and benzenes over a simulated fly ash showed the yield of PCDEs to be highly sensitive to the level of oxygen (Liu et al., 2011), and the homologue distribution profiles of PCDEs to be altered significantly by catalysts (Liu et al., 2013).

While PCDEs are noxious on their own right, they also act as precursors for the formation of the more toxic polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs). Irradiation (Norström et al., 1977) and thermal pyrolysis (Nito et al., 1997) of PCDEs yield appreciable concentrations of PCDD/Fs, especially PCDFs, with the formation of PCDD/Fs from PCDEs explained by Norström et al. (1977) and Nito et al. (1997) to proceed via intramolecular elimination of HCl and/or Cl_2. The work presented in this contribution will demonstrate that, this explanation is in fact incorrect. Likewise, the earlier study of Lindahl et al. (1980) emphasised similarities in the chlorination patterns of PCDEs and PCDD/F, prompting these researchers to assert, in agreement with other past investigations, that, the chlorination arrangement of produced PCDFs accords with a mechanism involving intramolecular elimination of HCl and/or Cl_2 operating during the transformation of PCDEs into PCDFs. The role of PCDEs as important intermediates for the formation of PCDFs was also highlighted by Onodera and Saitoh (1997) who found that, the thermal decomposition of chloronitrofen pesticide results in the formation of various congeners of PCDFs with a maximum yield of 0.5 mol% at 780 K. The authors postulated that, PCDFs arises from the removal of NO_2 group from chloronitrofen, formation of PCDEs, and the subsequent ring-closure of PCDEs into PCDFs. Despite these efforts, the exact mechanism that operates in the generation of PCDD/Fs from oxidation/pyrolysis of PCDEs remains elusive and subject to speculation.

To this end, the current contribution presents a detailed quantum chemical modelling of the mechanisms underlying the formation of PCDD/Fs from oxidation of PCDEs. The direct motivation behind this investigation originated from our curiosity to interpret experimental results of a recent study on the oxidation of the commonly used insecticide alpha-cypermethrin (Summoogum et al., 2013). We found that, oxidation of alpha-cypermethrin produces two types of PCDD/Fs precursors, namely chlorinated phenols/benzenes and PCDEs. The low concentrations of the one-ring species precursors and the chlorination patterns of PCDFs suggest that, PCDEs serve as active precursors for the formation of PCDD/Fs.

2. Computational details

All structural optimisations were carried out at the M062X/6-311 + G(d, p) level of theory, as implemented in the Gausian09 program (Frisch et al., 2009). The M062X (Zhao and Truhlar, 2008) is regarded as one of the most accurate functionals for deriving thermochemical and kinetic properties pertinent to general applications in organic systems. The extended basis set of 6-311 + G(3df, 2p) (Montgomery et al., 1994) served to obtain the reaction and activation enthalpies. Calculations of the intrinsic reaction coordinates (IRC) confirmed the nature of each transition structure and the ChemRate code (Mokrushin et al., 2002) facilitated the computation of the high-pressure rate constants for prominent reactions. Supplementary data provide energies, Cartesian coordinates, and vibrational frequencies for all considered structures. The RRKM theory, as implemented in the ChemRate code, yielded the pressure dependent rate constants for the prominent reactions. Reported reaction rate parameters follow a modified Arrhenius rate expression, $k(T) = AT^n \exp(-E^a/RT)$.

3. Results and discussions

It has been well-established that, mechanisms governing the formation of PCDD/FS are largely insensitive to degree and pattern of chlorination at *para* and *meta* sites of chlorophenols/chlorophenoxy radicals (Altarawneh et al., 2009). Depending on the pattern and degree of chlorination, there exist 209 distinct congeners of PCDEs, however, key mechanistic steps leading to the formation of PCDD/Fs from PCDEs primarily depend on the type of atomic substitution (i.e., hydrogen/chlorine) solely at the *ortho* positions. Presence of chlorine or hydrogen at *para* and *meta* sites exhibits negligible importance in pathways governing the generation of PCDD/Fs from PCDEs. Accordingly, we have elected to study decomposition and oxidation chemistry of the 2,2′-dichlorodiphenylether (2,2′-DCDE) molecule as a representative model compound for all congeners of PCDEs. As the 2,2′-DCDE molecule contains hydrogen and chlorine substituents at *ortho* sites in both aromatic rings, it can serve as a suitable surrogate for all DCDE congeners for investigating their transformations to PCDD/Fs.

Rotation of the ether bond in the 2,2′-DCDE molecule can result in several stable conformations. In Fig. S1 of the supplementary data, we present a rotor potential energy for internal rotation about the ether bond in the 2,2′-DCDE molecule. The presence of two local minima in Fig. S1 signifies the existence of two stable 2,2′-DCDE conformers. Structures of these two conformers are given in Fig. S2. The energy gap between these two conformers amounts to 3.7 kcal/mol. This marginal energy difference indicates the establishment of an equilibrium state between the two conformers at elevated temperatures, relevant to the formation of PCDD/Fs. Calculations in subsequent discussions are based on the most stable conformer (Conformer A in Fig. S2).

All reported energetic values refer to reaction and activation enthalpies computed at 298.15 K. Calculated thermochemical and kinetics values are thoroughly compared with analogous values from our recent study on the formation of brominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) from brominated diphenyl ethers (PBDEs) (Altarawneh and Dlugogorski, 2013), a commonly deployed type of brominated flame retardants. To simplify the discussion that follows, we label with symbols all intermediates in reaction mechanisms.

3.1. Formation of PCDFs from unimolecular decomposition of PCDEs

Fig. 1 displays reaction and activation enthalpies for pathways operating in the unimolecular decomposition of the 2,2′-DCDE molecule. Barrierless fission of C–Cl, C–H and C–O bonds requires endothermicities of 97.2 kcal/mol, 112.6 kcal/mol and 82.4 kcal/mol, respectively. Due to structural resemblance between PCDFs and PCDEs, direct elimination of HCl, and to a lesser extent H_2, followed by a ring-closure, represents the commonly proposed mechanism for formation of PCDFs during pyrolysis and oxidation of PCDEs (Lindahl et al., 1980). Calculated activation enthalpies for intramolecular elimination of HCl and Cl_2 amount to 83.4 kcal/mol

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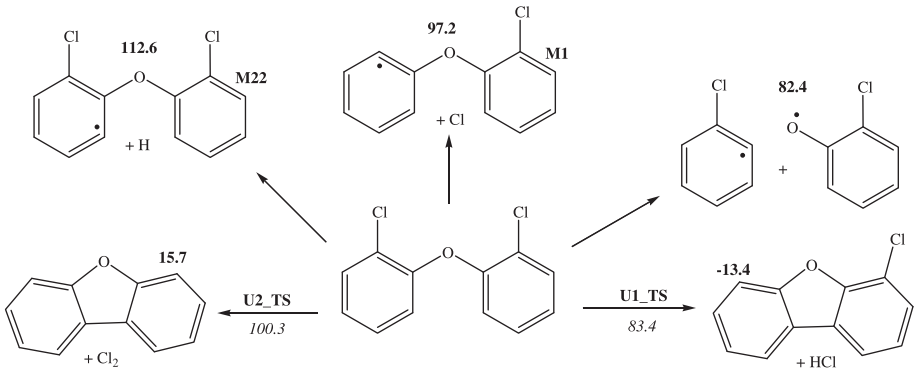

Fig. 1. Pathways involved in the unimolecular decomposition of 2,2′-DCDE. Values (kcal/mol) in bold and italic denote standard reaction and activation enthalpies at 298.15 K, respectively.

and 100.3 kcal/mol and take place via transition structures U1_TS and U2_TS, respectively. The exceedingly high enthalpic barriers for the formation of 4-monochlorodibenzofuran (4-MCDF) and dibenzofuran (DF) indicate that unimolecular corridors are of negligible importance in the transformation of PCDEs into PCDFs.

We fit a modified Arrhenius expression for intramolecular elimination of HCl and the subsequent formation of 4-MCDF, in the temperature interval of 400–1500 K and in the high pressure limit, to $k(T) = 1.32 \times 10^{10} T^{0.39} \exp(-42000/T)\, s^{-1}$. By employing the *A*-factor, for the fission of the ether linkage in non-chlorinated diphenyl ether, of $3.16 \times 10^{15}\, s^{-1}$ (van Scheppingen et al., 1997) and the calculated C–O bond dissociation in 2,2′-DCDE (81.2 kcal/mol), one deduces that, the rupture of the ether linkage dominates the unimolecular decomposition of 2,2′-DCDE at all temperatures. Nevertheless, the slow process of C–O bond fission inhibits formation of appreciable concentrations of chlorophenoxy and chlorophenyl radicals, which function as potent direct precursors for PCDD/Fs. The breakage of the ether linkage also governs the unimolecular decomposition of 2,2′-DBDE (Altarawneh and Dlugogorski, 2013). Thus, contrary to earlier interpretations of experimental measurements (Lindahl et al., 1980), the unimolecular decomposition of the 2,2′-DCDE molecule does not contribute to the inventory of PCDD/Fs in thermal systems.

3.2. Bimolecular reactions of 2,2′-DCDE with H and Cl radicals

Incineration of municipal waste often proceeds in a hydrogen-rich environment (Altarawneh et al., 2007a), as a consequence of the frequent release of hydrogen atoms from polymeric entities. Accordingly, reactions involving hydrogen atoms may control the combustion chemistry of PCDEs. Fig. 2a depicts plausible reactions of H atoms with the 2,2′-DCDE molecule. Addition/abstraction involving an *ortho* C(H) position represents analogous addition/abstraction at *meta* and *para* sites. As shown in Fig. 2a, the three addition channels incur very similar reaction enthalpies in the narrow range of 6.4–7.0 kcal/mol. Hydrogen and chlorine abstractions through the transition states TS_H1 and TS_H2 demand activation enthalpies of 15.7 kcal/mol and 13.2 kcal/mol, respectively. Addition at an *ortho* C(Cl) site results in the subsequent departure of a chlorine atom accompanied by exothermicity of 15.3 kcal/mol. Addition at C(H) and ether bridge sites (pivot carbon site) exhibits exothermicity of 22.9 kcal/mol and 21.4 kcal/mol and results in the formation of the M19 and M21 moieties. The slight enthalpic variance between TS_H1 and TS_H2 stems from the difference in the bond dissociation enthalpies of C–H and C–Cl bonds reported in Fig. 1. To enable extension of our kinetic analysis for all PCDEs congeners, Table 1 reports modified Arrhenius parameters for

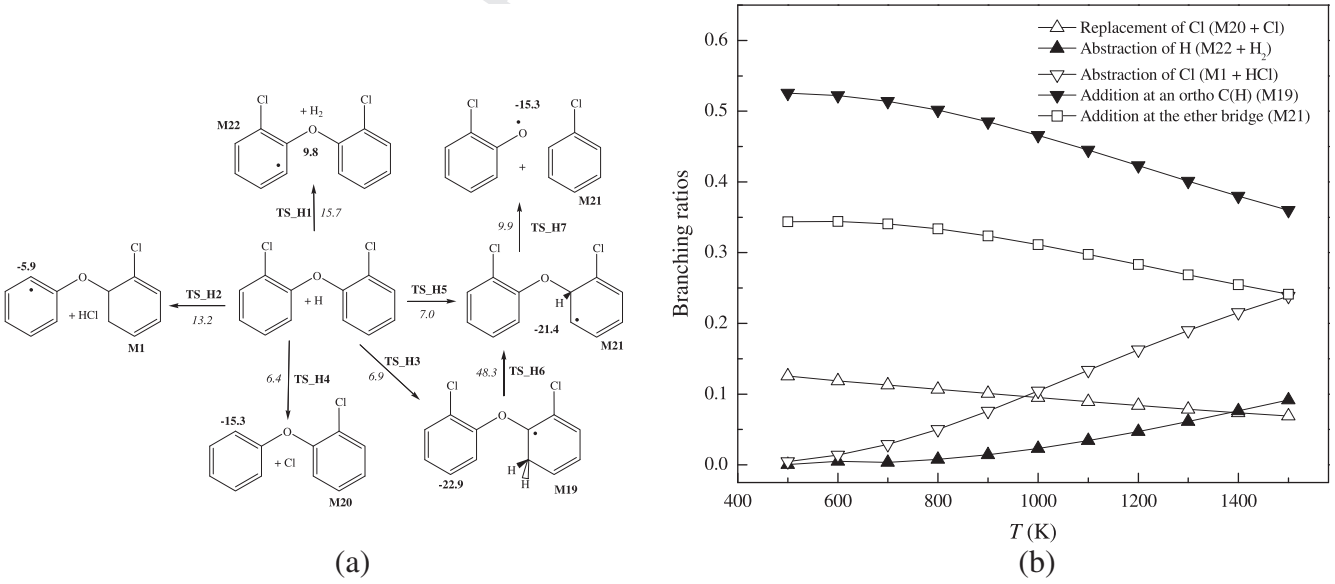

Fig. 2. (a) Reactions of H atoms with the 2,2′-DCDE molecule. Values (kcal/mol) in bold and italic denote standard reaction and activation enthalpies at 298.15 K, respectively, and (b) per-site branching ratios as a function of temperature for H + 2,2′-DBDE.

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Table 1
Fitted Arrhenius parameters (in temperature range 400–1500 K) for per site hydrogen atom reactions with the 2,2′-DCDE molecule. Values of A and Ea/R are in units of cm^3 molecule^{-1} s^{-1} and 1/K; respectively.

Reaction	A (s^{-1} or cm^3 molecule^{-1} s^{-1})	n	Ea/R (1/K)
HCl + M1	4.36×10^{-14}	1.54	6 700
M22 + H_2	2.51×10^{-15}	1.91	7 900
M20 + Cl	4.67×10^{-15}	1.38	3 500
M19	1.70×10^{-14}	1.44	3 600
M22	1.35×10^{-14}	1.42	3 600

H + 2,2′-DCDE reactions fitted in the temperature range of 400–1500 K per one abstraction/addition site. Based on these reaction rate constants, Fig. 2b plots branching ratios for all H + 2,2′-DCDE reactions. Addition at C(H) and pivot carbon sites dominates the overall reaction of H atoms with the 2,2′-DCDE throughout low and intermediate temperatures. Higher entropies of activation gradually increase the contribution of Cl abstraction channel.

As M19 and M21 adducts are important initial intermediates in the H + 2,2′-DCDE system, we further address their subsequent transformations. M19 intermediate either undergoes 1,2/1,3-hydrogen transfer reactions or ejects the out-of-plane H atoms; i.e., the reverse reaction of the addition of H to the 2,2′-DCDE molecule. A 1,2-hydrogen transfer via the reaction M19 → M21 proceeds through a sizable barrier of 48.3 kcal/mol (TS_H6). This barrier is significantly larger than the barrier of the reverse reaction (29.8 kcal/mol). Moreover, entropic factors favour the reverse reaction over isomerisation of M19 into M21. This finding infers the reforming of M19 into 2,2′-DCDE at all temperatures, which in turn diminishes the importance of H addition to C(H) sites. In contrary, fission of the ether linkage in M21 producing 2-chlorophenoxy radical and chlorobenzene holds more importance than the reverse reaction; viz., 9.9 kcal/mol (TS_H7) versus 28.4 kcal/mol (TS_H5). Accordingly, we expect reactions of H atoms with the 2,2′-DCDE molecule to be of crucial importance in mechanisms of PCDD/Fs formation from PCDEs, owing to the generation of the potent PCDD/Fs precursors – specifically, chlorophenoxy radical and chlorobenzene. In a previous theoretical study (Altarawneh et al., 2007b), we demonstrated that bimolecular reactions involving a chlorobenzene molecule and a 2-chlorophenoxy radicals produce various pre-intermediates for the formation of PCDFs via modest reaction barriers. Cyclisation of phenolic oxygen in these intermediates toward neighbouring *ortho* carbon atoms affords congeners of PCDFs.

The H + 2,2′-DCDE system thus exhibits a distinctive behaviour from that of the analogous system of H + 2,2′-dibromodiphenyl ether (2,2′-DBDE) (Altarawneh and Dlugogorski, 2013). In the latter, the formation of 2-bromophenoxy and bromobenzene displays negligible importance in comparison to the main channel of bromine abstraction.

Atomic chlorine is the most active chlorinating species of aromatic rings in comparison to other chlorine-containing species that exist in combustion media, namely, HCl, Cl_2 and OCl (Altarawneh et al., 2009). Gas-phase reactions of aromatic hydrocarbons with chlorine atoms proceed exclusively through H abstraction even at low temperatures; i.e., the addition corridor is of negligible importance (Alecu et al., 2007). The experimental work of Wiater and Louw (1999) on the reaction of chlorine atoms with diphenyl ether concluded that, addition at the *ipso* site (one of the two carbons carbon at the ether bridge C–O–C), which leads to rupture of the ether linkage, competes with hydrogen abstraction. Fig. 3a depicts the Cl + 2,2′-DCDE reaction channels. Abstraction of an *ortho* H atom proceeds through a trivial reaction barrier of 5.2 kcal/mol and produces M25 that resides 3.9 kcal/mol above the entrance channel. Due to its shallow well-depth, M25 readily dissociates at elevated temperatures into HCl and the M22 radical through a minor endothermicity of 5.9 kcal/mol. Thus, the enthalpy of the final products exceeds the energy of the transition state (9.8 kcal/mol versus 5.2 kcal/mol in reference to the initial reactants). It follows that, an accurate kinetic analysis for the abstraction reaction calls for the application of the variational transition state theory or the two-transition state theory. Nevertheless, an accurate rate constant for the net reaction (Cl + 2,2′-DCDE → M22 + HCl) could be obtained by setting the overall activation enthalpy of TS_Cl1 equal to the overall reaction enthalpy (9.8 kcal/mol). A per-site reaction rate constant for this bimolecular reaction corresponds to $k(T) = 4.07 \times 10^{-17} T^{2.57} \exp(-4500/T)$ cm^3 molecule^{-1} s^{-1}.

As illustrated in the lower part of Fig. 3a, the addition of chlorine at an *ipso* site splits the ether linkage in a two-step process. The first step features the formation of the short-lived complex M23. The complex is thermally unstable and forms the M24 adduct, which dissociates into 1,2-dichlorobenzene and 2-chlorophenoxy radical via a modest enthalpic barrier of 10.3 kcal/mol. By applying vibrational frequencies and rotational constants of (TS_Cl3) and its corresponding barrier height, we obtain a net rate constant for the bimolecular reaction (Cl + 2,2′-DCDE → 1,2-dichlorobenzene + 2-chlorophenoxy) as $k(T) = 1.30 \times 10^{-16} T^{1.92} \exp(-9800/T)$ cm^3 molecule^{-1} s^{-1}. Fig. 3b plots per-site branching ratios for the two channels operating in the reaction of chlorine atoms with 2,2′-DCDE. It is evident that,

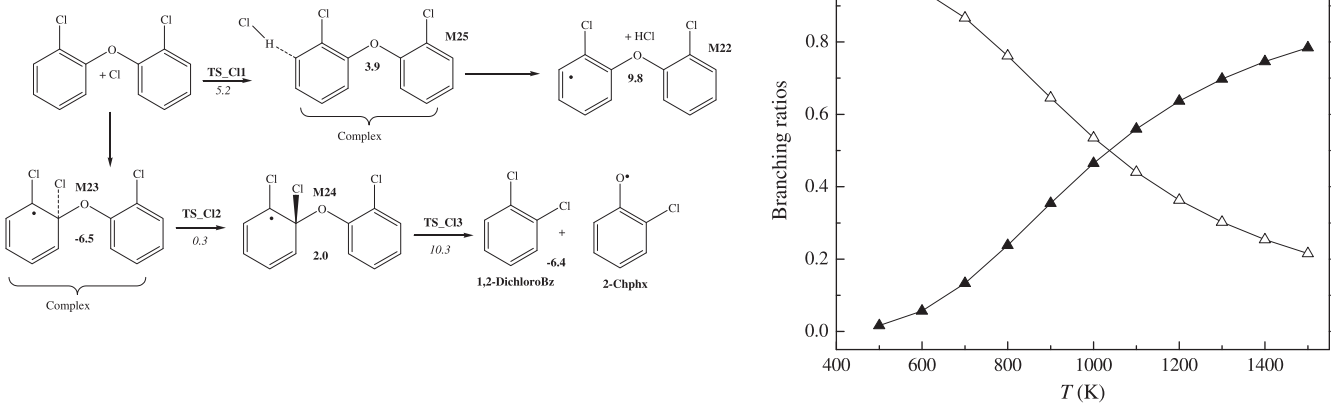

Fig. 3. (a) Reactions of Cl atoms with the 2,2′-DCDE molecule. Values (kcal/mol) in bold and italic denote standard reaction and activation enthalpies at 298.15 K, respectively, and (b) per-site branching ratios as a function of temperature for Cl + 2,2′-DCDE.

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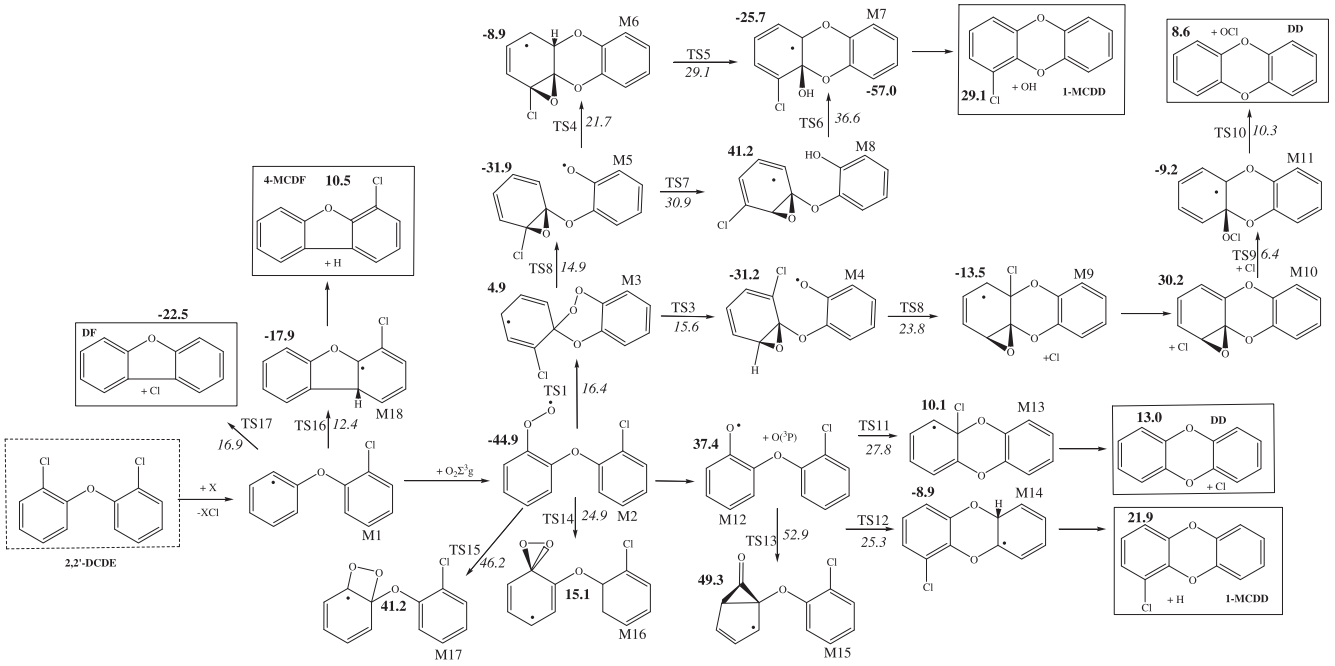

Fig. 4. Reaction mechanism for the oxidation of the 2,2′-DCDE molecule and the formation of DF, 4-MCDF, DD and 1-MCDD. Values (kcal/mol) in bold and italic denote standard reaction and activation enthalpies at 298.15 K, respectively.

hydrogen abstraction and splitting the ether linkage entail comparable rates, especially at the intermediate range of temperatures. This finding accords well with the experimental observation of Wiater and Louw (1999). The fact that *ipso* addition holds more importance than hydrogen abstraction at temperatures as high as 1000 K supports the results of the early work of Sidhu et al. (1995), who invoked the presence of chlorine atoms to explain the splitting of the ether bridge.

Reactions of bromine atoms with the 2,2′-DBDE molecule exhibit analogous behaviour; albeit, the cross-over temperature between hydrogen abstraction and *ipso* addition declines to 600 K. The rationale for this behaviour involves a remarkable difference in bond dissociation enthalpies between C and Cl bond in the 2,2′-DCDE molecule (97.2 kcal/mol) and C–Br in the 2,2′-DBDE (83.2 kcal/mol). The H-displacement (Cl + M20 → H + 2,2′-DCDE) demands a profound reaction enthalpy of 21.8 kcal/mol that marks negligible importance of this channel. Consequently, we excluded (Cl + M20 → H + 2,2′-DCDE) from our kinetic analysis. We conclude this section by observing that, the overall importance of the ether breakage channel increases with the degree of chlorination.

3.3. Formation of PCDD/Fs from 2,2′-DCDE

In view of the very high enthalpic values embedded in the unimolecular formation of PCDFs from 2,2′-DCDE molecule, it is highly unlikely that, direct intramolecular elimination of HCl/Cl_2 contributes to the formation of PCDFs from PCDEs. Moreover, rupture of the ether linkage proceeds too slowly to account for the establishment of the chlorophenoxy/chlorobenzene precursors. Accordingly, open-shell pathways become productive corridors in the transformation of PCDEs into PCDD/Fs. Fig. 4 demonstrates such pathways for the formation of DF, 4-MCDF, dibenzo-*p*-dioxin (DD), and 4-monochlorodibenzo-*p*-dioxin (4-MCDD) from the oxidation of 2,2′-DCDE.

In the last section, we have explained that, abstraction of *ortho* H/Cl atoms from PCDEs results in the formation of an *ortho*-centred phenyl-type radical in facile reactions. The leftmost part of Fig. 4 demonstrates that, the M1 phenyl-type radical initiates two ring-closure reactions leading to the formation of DF and 4-MCDF. Attachment of the apparent radical site in M1 to either chlorine or hydrogen bearing carbon atom, *ortho* to the oxygen bridge, necessitates modest activation enthalpies of 16.9 kcal/mol and 12.4 kcal/mol, respectively. Formation of DF molecule via the transition structure TS17 occurs simultaneously with the departure of the *ortho* chlorine atom in a exothermic reaction of 22.5 kcal/mol. Fission of the out-of-plane C–H bond in the M18 adduct takes place without encountering a reaction barrier and produces the 4-MCDF molecule. A lower enthalpic barrier of TS16 suggests a kinetic preference toward the formation of 4-MCDF from the 2,2′-DCDE molecule. Nevertheless, low enthalpic barriers of TS16 and TS17 indicate that even fully *ortho*-chlorinated congeners of PCDEs have capacity to form PCDFs.

The irreversible addition of an oxygen molecule to the radical site in M1 results in the formation of the stabilised peroxy-adduct of M2 with a profound exothermicity of 44.9 kcal/mol. The M2 intermediate branches into four competing channels. The first channel characterises direct fission of the peroxy O–O bond forming the phenoxy-type radical of M12 in an endothermic reaction of 37.4 kcal/mol. The M12 adduct could also be sourced from bimolecular reactions involving the parent M1 intermediate with other species that exist in combustion media. The TS13 starts the so-called ring contraction/CO elimination mechanisms from the M12 adduct. However, the elevated reaction enthalpy of 52.9 kcal/mol hinders this process. Alternatively, M12 isomerises into M13 and M14 intermediates via modest activation enthalpies of 27.8 kcal/mol (TS11) and 25.3 kcal/mol (TS12), respectively. The loss of the out-of-plane Cl and H atoms from M13 and M14 intermediates produces DD and 1-MCDD. In an analogy to the well-studied system of phenylperoxy, isomerisation of M2 into the 1,1-dioxiranyl-type radical (M16) and 1,2-dioxetanyl-type radical (M17) demands activation enthalpies of 24.9 kcal/mol (TS14) and 46.2 kcal/mol (TS15), correspondingly. Elimination of a CO_2 molecule in a two-step process dominates the fate of M16.

Bridging the outer atom at the pivot carbon of the neighbouring phenyl ring marks the lowest energy pathway among the four initial exit channels of M2 and results in the production of the

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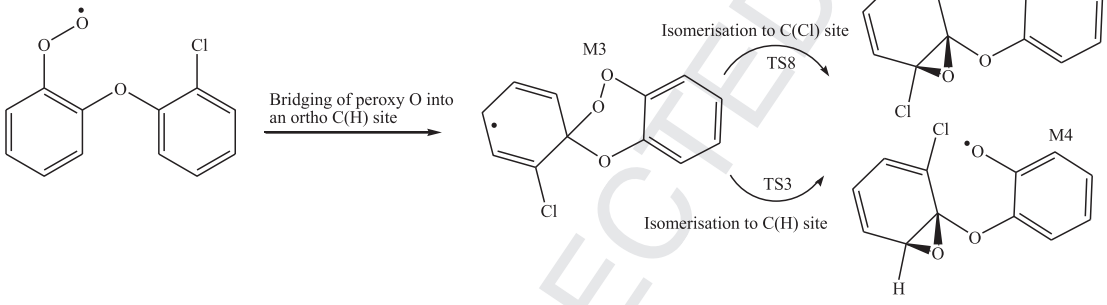
three-membered-ring structure of M3. Calculated reaction enthalpy for this reaction amounts to 16.4 kcal/mol (TS1). The M3 adduct forms the two oxirane-type structures M4 and M5 through very comparable low activation enthalpies of 15.6 kcal/mol (TS3) and 14.9 kcal/mol (TS8). In view of their considerable exothermicity (31.2 kcal/mol and 31.9 kcal/mol), isomerisation of M3 into M4 and M5 approximates an irreversible process. The pre-dioxin intermediate M7 evolves from the M5 adduct through ring-closure (M5 → M6) and intramolecular transfer (M6 → M7). Calculations yield enthalpic barriers for these two reactions of 21.7 kcal/mol (TS4) and 29.1 kcal/mol (TS5), respectively. Expulsion of an OH group from the M7 intermediate affords the 1-MCDD molecule. The M7 intermediate could also form by transfer of an H atom from a phenyl ring into the phenoxy O atom (M5 → M8) followed by a ring-closure (M8 → M7). As shown in the middle part of Fig. 4, a DD molecule develops from the M4 intermediate in a similar reaction sequence, involving comparable activation enthalpies. The initial oxidation of the M2 intermediate to produce DD and 1-MCDD molecules constitutes the most accessible exit channel – a striking feature of Fig. 4. All reactions explained in Fig. 4 require modest activation enthalpies. As an illustrative example for the facile nature of the oxidative transformation of PCDEs into PCDDs, the net activation enthalpy for the formation of 1-MCDD from M2 requires a value of 19.8 kcal/mol and the final products (1-MCDD + OH) reside 32.5 kcal/mol below the M2 adduct. Clearly, the reaction sequence:



represents a bottle-neck for the entire complex mechanism demonstrated in Fig. 4. The comparable activation enthalpies of TS4 and TS5 demonstrate insensitivity of isomerisation of M3 into oxirane intermediates (M4 and M5) to the type of atomic substitutions. Even fully chlorinated PCDEs proceed in very exothermic reactions to yield PCDDs. Table 2 lists rate constants for these three most important reactions at the high-pressure limit and at 1 atm. It is insightful to stress that, loss of an *ortho* H or Cl atom from PCDEs represents a prerequisite for the generation of PCDD/Fs. Oxidation starting at *para* or *meta* site produces a five-membered ring structure and does not contribute to the formation of PCDD/Fs. Because of minimal differences in values of reaction and activation enthalpies, the formation of PCDD/Fs from PCDEs exhibits very similar mechanistic and energetic features to the analogous formation of PBDD/Fs from PBDEs (Altarawneh and Dlugogorski, 2013).

In order to confirm that mechanisms governing transformation of PCDEs into PCDD/Fs are largely insensitive to degree and patterns of chlorination, Table S1 in the supplementary data compares reaction and activation enthalpies between systems of 2,2′-DCDE and 2,2′,4,4',6,6'-HexaCDE for three selected reactions; namely M2 → M3, M3 → M5 and M1 → DF/2,4,6,8-TetraCDF + Cl. As shown in Table S1, calculated values for the two systems are within 1.0–3.0 kcal/mol. It follows that, all PCDEs are expected to exhibit very similar kinetic and mechanistic characteristics in their oxidative transformation into PCDD/Fs. It is worthwhile mentioning that, the final homologue profile of PCDD/Fs not only depends on the parent PCDEs precursors but also on subsequent chlorination/dechlorination reactions.

Table 2
Fitted Arrhenius parameters (in temperature range 400–1500 K) at the high-pressure limit and at 1 atm for prominent unimolecular reaction in the oxidative transformation of PCDEs into PCDDs. Values of A and Ea/R are in units of s^{-1} and 1/K; respectively.

Reaction	High-Pressure			1 atm		
	A	n	Ea/R	A	n	Ea/R
M1 → M3	1.38×10^{10}	0.25	8700	5.50×10^{10}	0.00	8800
M3 → M4	7.60×10^{11}	0.52	7700	3.98×10^{29}	−5.41	9800
M3 → M5	1.22×10^{12}	0.51	8000	5.37×10^{30}	−5.78	10300

4. Conclusions

This study reports mechanistic, energetic, and kinetic information pertinent to the formation of PCDD/Fs from PCDFs. We have found that, all plausible unimolecular decomposition pathways of the 2,2′-DCDE molecule incur very high reaction and activation enthalpies in the range of 82.4–112.6 kcal/mol. HCl formation and rupture of the ether bridge hold comparable importance in the bimolecular reactions of the 2,2′-DCDE molecule with H and Cl atoms. Loss of an *ortho* H or Cl atoms from the 2,2′-DCDE molecule leads to the formation of DF and 4-MCDF in a facile ring-closure reactions. We have shown that, an *ortho* peroxy-type adduct (RO_2) evolves via a series of exothermic reactions to yield PCDDs. Results presented herein clearly support our earlier experimental findings that PCDEs act as potent precursors for PCDD/Fs on their own right; i.e., without necessity to form chlorophenoxy/chlorobenzene dioxins building blocks.

Conflict of interest

The authors declare no conflict of interest.

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Appendix A. Supplementary material

Appendix A, titled Cartesian coordinates, total energies and vibrational frequencies for all structures, documents the

supplementary data related to this article. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere. 2014.04.027.

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